GEOCHEMICAL CHARACTERIZATION OF THERMAL AND COLD GROUNDWATERS OF METHANA PENINSULA (PELOPONNESUS, GREECE)

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Abstract: A comprehensive hydrogeochemical study of the cold and thermal groundwaters of the presently quiescent volcanic system of Methana was undertaken collecting 59 natural water samples during the period 2004-2007. Methana is a peninsula whose climatology and hydrology can be compared to the nearby small islands of the Aegean Sea. Similarly the chemical and isotopic composition of its water is dominated by the mixing of seawater with meteoric water. But the simple mixing trend is modified by water-rock interaction processes, enhanced by the dissolution of endogenous CO_2, leading to strong enrichments in Alkalinity, Calcium, Barium, Iron and Manganese.

1. Introduction

Methana is a peninsula of about 44 km^2 extension at the north-eastern coast of Peloponnesus in Greece. It could almost be considered as an island, being joined to the mainland by an isthmus, which is only 300 m wide. It has no perennial springs or streams and according to Pantelouris (1980) it belongs to the southeastern driest region of Greece with an annual rainfall of less than 400 mm. Therefore, being water shortage in this area very common, no wonder that in geographic literature, Methana is often described as "a rough and rocky place" (Miliarakis 1886, quoted in Mee and Forbes 1997). Its hydrology can be better compared to the arid islands of the nearby Cyclades archipelago (Dazy *et al*. 1997) than to the Peloponnesus to which it geographically belongs. Notwithstanding these harsh conditions, the peninsula has a long settlement history starting from prehistorical times. Stable human presence was archeologically documented since the Early Helladic period at the end of the IV millennium B.C. (Mee and Forbes 1997). Fertility of its young volcanic soils was probably one of the main reasons that attracted its earliest inhabitants. Contrasting to the neighbouring parts of the Peloponnese the rocks outcropping at Methana are mostly of volcanic origin. The only exceptions are found to the northwest (hill of Panagia) and to the south (Asprovouni of which the isthmus is a prolongation) where Mesozoic limestones crop out (Dietrich and Gaitanakis, 1995). Volcanic activity produced mainly lava domes and lava flows, generally of andesitic composition, and only few pyroclastic deposits of limited extent (Pe-Piper and Piper 2002). The whole peninsula has a mountainous relief with the highest altitude reached at Chelona (740 m). Flat land is rare, limited to a few upland basins and restricted coastal plains. Therefore during its millennial settlement history more than the half of its entire surface has been covered with terraces permitting cultivation of the mountains' slopes. Terraces were built generally up to altitudes of about 400 m but in the central mountainous area they extend to above 600 m (James *et al*. 1997). Such a huge work permanently modified the geomorphology of the peninsula allowing widespread agricultural exploitation and protecting its slopes from fast erosive processes. For centuries agricultural production was limited to products that needed no irrigation, mainly wine and olives. The situation deeply changed during the first half of the 20th century when many irrigated crops were introduced. Such drastic change was due to a series of concurring factors: the favourable climate for the production of early crops, the closeness to the important and fast growing consumer market of Athens and the motorization of the ships allowing a regular and

secure transport to the market (Forbes 1997). To obtain the necessary irrigation water, in those years many wells were sunk down to the groundwater table in areas close to the coast. The water of these wells, which were up to 20 m deep, was brought to the surface through an endless chain of buckets operated by animal power (donkeys or mules). Although, after the installation in the 1960s of a pipeline bringing water through the isthmus from the nearby plain of Troezen, the problem of an adequate water supply was solved, many of the wells excavated in that period are still in use for irrigation even if operated now with electrically powered pumps.
The youth of the volcanic system of Methana, apart from the historic activity that emplaced the dome and lava flows of Kammeno Vouno in 230 B.C., is also testified by the presence of hydrothermal manifestations (Pe-Piper and Piper 2002). The exploitation of the thermal springs, which begun in Roman times (Mee and Forbes 1997), represents nowadays another important economic income for its inhabitants.
Apart from sparse chemical analyses published in previous years (Pertessis 1925; von Leyden 1940; Minissale *et al*. 1997) no comprehensive study of the cold and thermal groundwaters of Methana exists in the scientific literature. In this paper we present new chemical and isotopic analyses of many groundwater samples collected on the peninsula during the period 2004-2007 with the aim of describing the main geochemical processes responsible for their composition.

2. Methodology

During the period Dec. 2004 – May 2007, 59 groundwater samples were collected on the peninsula of Methana (Figure 1 and Table 1). Sixteen samples were taken from the thermal springs (samples 1 to 16 in Table 1), 39 from the cold aquifer (17 to 55) and 4 from rainwater harvesting systems (56 to 59). The latter were collected to get insight on the chemical and isotopic composition of the meteoric recharge. The cold groundwater samples were taken from many of the well dug on the peninsula. Where possible the sample was collected through the pump, otherwise a sampling bottle was lowered to the water table.
Water temperature, pH and electric conductivity were measured in the field with portable instruments. Chemical and isotopic analyses were carried out at the laboratories of the INGV-Palermo. Total alkalinity was determined by titration with 0.1 M HCl on unfiltered samples. Major anions (Cl^-, NO_3^- and SO_4^{2-}) were determined by ionic chromatography on filtered samples. Major cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) by ionic chromatography and minor elements (B, Li, Rb, Sr, Ba, Fe and Mn) by ICP-MS were quantified on filtered and acidified (0.2% HNO_3) samples. Oxygen and hydrogen isotopic composition of the water was determined by mass-spectrometry on unfiltered samples and expressed in ‰ with respect to the international standard V-SMOW.

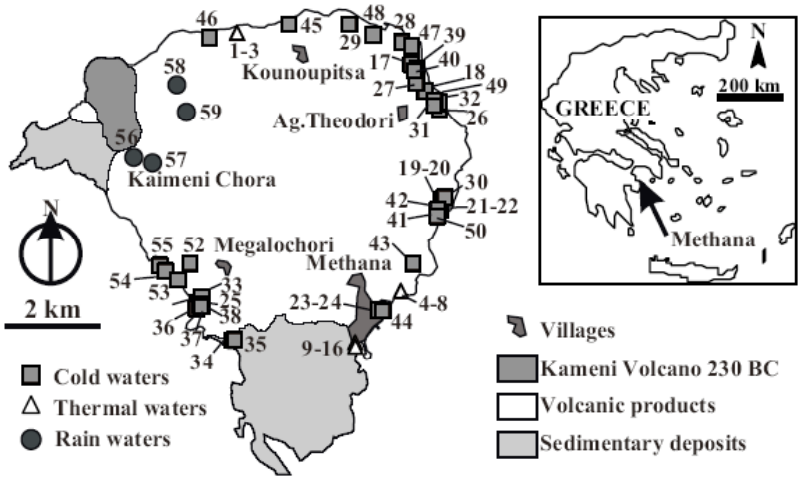

Figure 1 – Simplified geological map of Methana and location of the sampling sites

Table 1. Results of chemical and isotopic analyses of the water samples. Numbers as in Fig. 1.

N	date	T °C	pH	cond	Na	K	Mg	Ca	Cl	NO_3	SO_4	Alk	Li	B	Mn	Fe	Rb	Sr	Ba	$\delta^{18}O$	δD
				µS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	‰	‰
1	01/12/2004	24.6	6.42	34700	7476	264	840	743	13734	< 1	1721	1168	419	5111	123	28.6	158	5617	29.6	-1.0	-7
2	23/06/2006	30.1	6.09	50000	10039	384	1075	908	18316	< 1	2186	1696	643	7529	1111	71.4	277	8158	54.6	-0.5	-5
3	13/09/2006	30.9	6.11	32400	11028	406	1206	1009	20503	< 1	2457	1385	671	7842	989	45.4	297	9152	72.1	0.2	-3
4	01/12/2004	27.5	6.72	13000	2327	112	308	385	4018	< 1	681	1141	nd	nd	nd	nd	nd	nd	nd	-5.0	-27
5	08/11/2005	34.0	6.63	12800	2548	126	307	419	4305	< 1	727	1226	558	2727	773	16.2	309	2726	7.57	-5.2	-29
6	24/06/2006	37.3	6.08	15700	2128	112	277	395	3673	< 1	629	1162	463	2319	64.0	87.1	262	2210	11.9	-5.7	-32
7	13/09/2006	37.5	6.32	10200	2669	136	341	464	4686	< 1	745	1232	576	2985	911	12.6	344	3010	4.91	-5.3	-31
8	26/05/2007	36.0	6.35	13100	2527	132	310	398	4454	< 1	668	1229	563	2909	697	31.8	328	2899	5.49	-5.4	-28
9	01/12/2004	30.0	6.00	23300	4395	215	520	467	8039	37.5	1096	982	663	3867	495	40.1	338	3686	25.8	-3.5	-20
10	01/12/2004	29.7	5.80	48000	10279	454	1154	879	19329	< 1	2495	1071	nd	nd	nd	nd	nd	nd	nd	0.7	2
11	08/11/2005	30.5	6.16	26900	5669	277	614	558	10376	25.4	1308	942	927	5557	854	36.7	478	5027	40.0	-2.8	-17
12	08/11/2005	30.9	6.13	50500	11582	541	1253	1032	21442	< 1	2721	1098	1728	11470	2796	nd	961	10180	71.2	1.1	3
13	24/06/2006	33.5	5.82	58000	9499	457	1053	966	17712	< 1	2398	976	1591	10470	2380	758	955	9496	66.9	-0.7	-7
14	26/05/2007	32.1	5.98	30100	10040	451	1073	821	17490	< 1	2120	1034	1602	10330	2822	94.0	988	10570	60.0	-0.1	-4
15	26/05/2007	33.1	5.98	46000	11712	556	1349	1026	22034	< 1	2595	1037	1736	11840	3276	97.3	1074	11340	66.0	1.3	5
16	26/05/2007	30.1	6.43	46800	11579	524	1287	917	21378	< 1	2548	964	1480	10620	2700	92.5	903	10860	58.5	1.1	4
17	08/11/2005	18.0	8.10	2150	252	13.3	53.3	83.8	448	3.72	72.5	311	45.8	161	1.56	5.19	9.73	462	207	-5.6	-29
18	08/11/2005	17.0	7.31	1365	143	15.6	53.9	85.8	277	40.2	109	275	4.20	81.3	1.32	2.65	14.1	446	294	-5.9	-31
19	24/06/2006	16.5	6.30	734	49.9	21.1	20.9	66.3	53.5	9.30	35.5	326	5.93	162	52.8	64.7	8.03	264	79.0	-4.5	-24
20	11/09/2006	18.0	6.31	739	49.7	21.5	22.6	78.2	56.4	4.96	31.2	375	8.69	177	338	388	8.88	327	87.5	-4.7	-25
21	24/06/2006	20.3	6.59	4110	688	73.5	147	219	1234	29.1	55.2	1129	365	3257	7.81	4.86	131	1426	319	-6.1	-34
22	26/05/2007	19.1	6.66	4740	716	73.9	165	193	1298	< 1	35.0	1251	489	3715	20.0	46.2	161	1735	329	-5.8	-32
23	25/06/2006	22.2	5.95	1460	169	22.3	36.0	118	200	167	107	360	34.8	612	1.01	3.17	29.4	617	89.0	-6.9	-39
24	27/05/2007	21.5	5.89	1150	120	19.9	31.0	98.0	109	115	82.1	400	40.0	327	1.48	4.36	28.5	574	63.8	-6.3	-38
25	25/06/2006	18.1	6.44	5210	863	37.9	182	277	1670	23.8	257	793	38.1	447	4.73	96.2	33.2	1329	387	-6.7	-40
26	25/06/2006	18.3	7.49	1170	168	10.6	40.5	74.7	327	4.96	59.5	232	17.3	84.3	7.74	3.89	4.42	415	130	-6.1	-34
27	25/06/2006	20.2	7.19	1980	274	14.1	89.7	97.2	542	4.34	67.7	506	53.8	162	4.15	9.18	11.4	588	206	-6.2	-34
28	25/06/2006	19.1	7.27	2340	389	21.9	71.9	82.6	748	< 1	97.0	250	36.1	196	69.5	42.0	14.4	627	134	-6.4	-35
29	25/06/2006	21.0	6.98	2110	255	12.9	114	114	517	4.96	75.4	610	6.91	157	3.11	13.9	11.0	679	167	-6.7	-35
30	11/09/2006	18.5	6.98	1603	217	17.6	44.7	152	343	4.34	48.0	613	10.9	279	1298	331	7.67	687	189	-3.8	-21
31	11/09/2006	18.7	7.51	1439	189	16.0	40.2	113	399	1.24	106	232	4.63	114	195	30.1	8.18	679	102	-5.5	-27
32	11/09/2006	20.3	6.80	7800	1281	72.3	192	146	2373	38.4	399	174	4.62	486	7.33	112	63.4	1278	297	-6.0	-31
33	11/09/2006	21.8	6.36	2400	320	19.2	115	201	694	22.1	115	750	51.2	260	8.95	68.1	19.2	876	169	-7.1	-40
34	11/09/2006	20.5	7.60	2840	492	12.9	63.3	183	988	9.92	145	299	0.95	166	4.17	39.7	6.69	507	187	-7.0	-41
35	11/09/2006	18.9	7.02	1633	237	9.38	37.1	138	484	4.84	73.0	299	0.98	111	28.5	82.9	4.45	338	115	-7.4	-42
36	12/09/2006	21.1	6.95	2660	411	25.8	145	236	776	21.1	109	1049	114	359	118	33.9	25.4	1038	166	-6.6	-39
37	12/09/2006	21.5	6.32	3540	701	37.9	178	259	1347	45.9	195	997	102	468	1.51	8.59	40.9	1278	208	-7.1	-41
38	12/09/2006	21.0	6.60	1168	137	6.26	35.0	102	225	14.9	108	299	3.63	113	3.13	7.42	7.81	597	46.8	-6.9	-41
39	12/09/2006	21.6	7.83	2530	530	21.1	77.8	134	782	47.7	279	500	52.9	176	nd	5.43	20.4	776	146	-5.8	-33
40	12/09/2006	22.5	7.15	2100	338	14.1	79.8	110	661	17.4	98.4	351	53.2	172	1.50	6.34	12.4	740	258	-6.4	-35
41	13/09/2006	21.6	8.06	4660	1067	117	199	273	2044	17.3	0.48	1214	582	4995	1659	605	102	2307	515	-1.7	-11
42	13/09/2006	22.2	7.26	4320	971	53.2	225	178	2218	4.96	22.1	421	176	2576	137	2086	62.0	1389	474	-2.7	-14
43	13/09/2006	24.4	7.04	5840	1441	41.8	247	424	3067	< 1	380	592	104	808	56.2	66.1	33.0	3089	230	-6.2	-33
44	13/09/2006	22.5	6.10	1632	203	25.0	60.3	172	270	55.6	101	726	45.0	1544	333	9.02	39.7	778	108	-6.5	-38
45	13/09/2006	22.0	7.32	2170	356	30.9	66.6	134	712	15.3	172	238	1.68	215	9.53	4.54	17.2	703	232	-6.1	-35
46	13/09/2006	26.0	7.35	2830	492	30.1	87.2	83.8	900	2.98	101	354	76.6	434	365	449	42.7	619	66.7	-6.5	-34
47	26/05/2007	19.1	7.43	5570	701	21.5	110	247	1357	< 1	240	543	0.60	238	2697	87.1	13.6	1410	150	-5.4	-32
48	26/05/2007	18.0	7.58	907	99.3	9.38	30.7	40.3	212	8.68	42.2	134	6.79	65.6	3.41	4.88	9.04	262	87.7	-6.4	-35
49	26/05/2007	18.1	7.26	1005	116	7.04	35.4	63.3	235	1.86	47.5	220	18.3	70.4	1.78	4.45	3.63	359	110	-6.5	-35
50	26/05/2007	19.8	8.32	7480	1358	116	214	170	2548	< 1	4.32	1098	563	5825	848	295	133	2193	657	-0.8	-12
51	27/05/2007	19.6	6.52	4800	607	27.8	158	233	1111	17.4	143	967	117	427	10.1	9.61	28.5	1192	131	-6.8	-38
52	27/05/2007	19.7	6.40	3870	553	25.4	151	222	1027	18.6	132	946	115	405	20.5	17.5	29.1	1152	105	-6.8	-38
53	27/05/2007	18.1	7.00	1276	134	9.38	49.5	106	238	6.82	48.5	451	11.5	121	1.45	4.69	14.5	601	49.0	-6.6	-39
54	27/05/2007	19.2	6.97	3950	609	30.9	142	211	1212	1.86	170	662	73.2	510	27.4	25.6	27.5	1321	163	-6.2	-37
55	27/05/2007	20.0	6.44	2900	473	18.0	99.9	93.6	850	9.30	103	458	85.8	345	2.37	7.08	20.4	641	26.7	-6.8	-39
56	25/06/2006	18.1	7.97	305	14.3	3.52	6.68	49.3	16.3	44.0	57.6	85	nd	nd	nd	nd	nd	nd	nd	-6.9	-38
57	25/06/2006	15.7	7.66	200	9.20	8.60	2.07	41.5	10.3	< 1	0.96	153	nd	nd	nd	nd	nd	nd	nd	-7.1	-38
58	25/06/2006	18.1	8.37	198	5.52	2.74	1.22	44.9	9.22	< 1	10.1	134	nd	nd	nd	nd	nd	nd	nd	-7.4	-42
59	25/06/2006	19.2	7.49	260	11.5	17.2	2.31	46.9	11.7	1.49	13.9	177	nd	nd	nd	nd	nd	nd	nd	-6.9	-37

3. Results and discussion

3.1. Stable isotopes

Isotopic composition of the analysed waters range from –7.4 to 1.3 ‰ for $\delta^{18}O$ and from –42 to 5 ‰ for δD. At present we have no isotopic data on the meteoric recharge on the peninsula. Indeed also precipitation amount data are presently lacking. The only data (600 and 390 mm for the agricultural season 1972-73 and 1973-74 respectively) are found in James *et al*. (1997). To get some insight in the isotopic composition of the meteoric recharge at Methana we can use both the data of the samples collected in the rainwater harvesting systems (RHSs) and the literature data of the nearby Athens region (Argiriou and Lykoudis 2006). On a δD-$\delta^{18}O$ plot (Fig. 2a), the points representative of the RHSs fall between the global meteoric water line ($\delta D=8\times\delta^{18}O+10$) and the East Mediterranean meteoric water line ($\delta D=8\times\delta^{18}O+22$) defining a local meteoric water line (LMWL - $\delta D=8\times\delta^{18}O+18$), which is typical for the central Mediterranean region (D'Alessandro *et al*. 2004). On the other side rainwaters of the Athens region (Argiriou and Lykoudis 2006) define a LMWL ($\delta D=7.3\times\delta^{18}O+11.4$), which is not statistically different from that obtained from the RHSs data. Most of the cold groundwaters plot close to the two above defined LMWLs evidencing a prevailing origin through meteoric recharge. On the contrary the thermal waters and some of the cold groundwaters define a mixing line whose end-members are the Aegean sea water (Gat *et al*. 1996) and the local meteoric recharge (Fig. 2a). Seawater intrusion is a quite common problem in coastal aquifers, especially in arid environments where overexploitation can easily exacerbate this process (Dazy *et al*. 1997). Furthermore, geothermal systems developed close to the coast display nearly always a prevailing seawater component. In this case seawater intrusion is generally independent from anthropogenic causes, being mainly related to convective movements of the geothermal fluids within the reservoir (Grassi *et al*., 1995; Celico *et al*., 1999). Moreover, at Methana, only naturally escaping thermal waters are currently exploited.
On a Cl-$\delta^{18}O$ diagram (Fig. 2b), while thermal waters still define a mixing line between the Aegean seawater and the local meteoric recharge, some of the cold groundwaters plot well above this line. These samples were collected from very shallow wells (1 – 5 m), not exploited and whose large diameter allows an easy exchange with atmosphere. The most probable process that could explain their peculiar composition is an intense evaporation. But also other wells, although deeper and still exploited, show some clues of evaporation (i.e. low deuterium excess) plotting a little bit above the seawater-meteoric water mixing line.

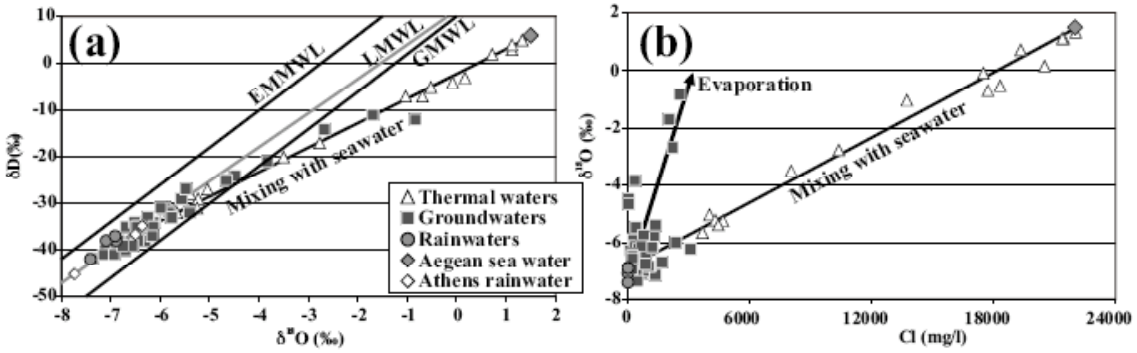

Figure 2 – δD-$\delta^{18}O$ (a) and $\delta^{18}O$-Cl (b) binary diagrams. EMMWL = East Mediterranean meteoric water line (Gat and Carmi, 1970), LMWL = local meteoric water line (Argiriou and Lykoudis, 2006), GMWL = global meteoric water line (Craig, 1961).

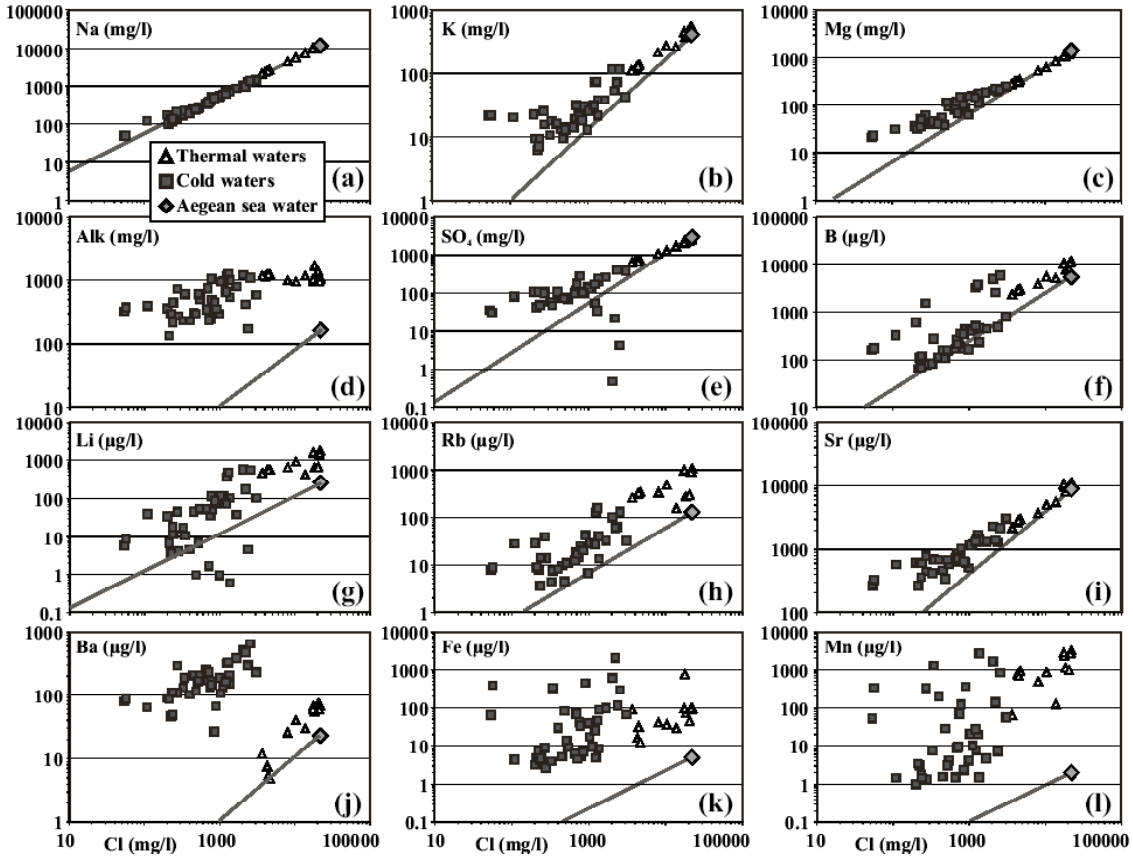

Figure 3 – Chlorine vs. (a) Na, (b) K, (c) Mg, (d) Alkalinity, (e) SO_4, (f) B, (g) Li, (h) Rb, (i) Sr, (j) Ba, (k) Fe and (l) Mn binary diagrams. Grey line represents the ion/Cl ratio of seawater.

3.2. Chemical composition

The influence of seawater on both thermal and cold groundwaters can be also highlighted on a Na-Cl diagram (Figure 3a) where nearly all samples plot on the line representing the Na/Cl ratio of the Aegean seawater. Such influence can be due not only to direct seawater intrusion both in the thermal and cold aquifer but also to the contamination of the meteoric recharge through sea-spray. The first process is probably responsible for the most part of the dissolved load in the waters displaying the highest salinity while for the most diluted ones the second process becomes significant. The contribution of sea-spray in small islands (to which Methana can be compared) through meteoric recharge has recently been evidenced in the Aegean area (Dazy *et al*. 1997). The samples collected in RHSs display Na and Cl values in the range of composition of rainwaters collected close to the coast but lower than those measured on the Aegean islands (Dazy *et al*. 1997). This could be due to the fact that all sampled RHSs were located in places not directly open to the sea. But part of the recharge areas feeding the aquifers of Methana are more exposed to sea-spray deposition and, due to the dry climatic conditions, the infiltrating waters could probably be further concentrated by evaporation processes before infiltration.
In the salinity range of the analysed waters chloride behaves as a conservative ion, which is not affected by precipitation of secondary minerals in the aquifers. For this reason its concentration was compared with all other analysed ions in binary diagrams to get insight on processes affecting the mineralization of the waters (Figure 3). The obtained ion/chloride ratios are nearly always higher than the respective ion/chloride ratio in seawater. This testifies that the total ionic content of the water doesn't derive exclusively from mixing between the seawater and meteoric water end-members. Water-rock interaction processes within the aquifer, further enhanced by increased water aggressiveness due to the dissolution of endogenous CO_2 (D'Alessandro *et al*.

2007), are responsible for the enrichment of nearly all analysed ions. The influence of CO_2 dissolution in the aquifer is also confirmed by the high alkalinity (Figure 3d) and CO_2 partial pressure values (D'Alessandro *et al*. 2007) measured especially in the thermal waters. Aggressiveness of the thermal waters is possibly further enhanced by the addition of H_2S of hydrothermal origin and by the proton release in its oxidation reaction in the shallowest part of the aquifer. This process cannot be confirmed by the present data and, as we will see below, a significant part of the dissolved SO_4 derives from sulphate minerals dissolution.

Iron and manganese are among of the most enriched elements (Figures 3k and 3l). They derive from the incongruent dissolution of femic minerals in the volcanic rocks of Methana. Such strong enrichment is often found in the geothermal systems along the south Aegean arc. For example thermal springs at Santorini and Milos islands, discharging directly in the sea, are renown for their high content in these elements (Boström *et al*. 1990; Cronan and Varnavas 1999). In these springs, the mixing with open seawater produces abundant precipitation of a Fe and Mn enriched sediment. Also at Methana Fe and Mn enriched sediments were found close to its coasts evidencing past and/or present underwater hydrothermal activity (Hübner *et al*. 2004).

Some few exceptions of the enrichment with respect to the ion/chloride ratio of seawater can be found in the Mg, Li and SO_4 contents of some of the sampled waters. In the case of Mg (Figure 3c), only the most saline thermal waters display a small depletion that can be attributed either to the incorporation of Mg in secondary minerals or to dolomitization processes within the thermal aquifer. The depletion of SO_4 (Figure 3e), sometimes nearly reaching the disappearance, affects only a few cold water samples. These samples were collected in the same wells in which the isotopic composition highlighted important evaporative processes. In these shallow wells the decay of accumulated organic debris probably causes strongly negative redox potentials leading to the reduction of SO_4 to H_2S. The latter escapes in gaseous form during evaporation processes or precipitates as sulphide minerals leaving the water sulphur depleted.

Among the major cations, calcium is the most enriched with respect to the ion/chloride ratio of seawater (Figure 4a). Apart from dissolution of primary minerals in volcanic rocks the high calcium content could derive from carbonate rocks. Only two of the sampled well (samples 34 and 35) were excavated where Mesozoic carbonate rocks crop out and two of the thermal springs (samples from 9 to 16) emerge at the contact between volcanics and limestones, but geophysical investigation highlighted the presence of carbonate rocks under the volcanic products of the peninsula (Volti 1999). The carbonate rocks extend under the whole peninsula at depths never exceeding about 1 km, and at least the aquifers feeding the thermal springs are partially composed of these rocks.

In the Ca vs. Alkalinity binary diagram (Figure 4b) most of the cold groundwaters plot along a line corresponding to the stoichiometric ratio of calcium carbonate dissolution. This could be due to dissolution of either limestones or calcite vein within the volcanic rocks. Important calcite mineralizations have been found in many hydrothermally altered volcanic rocks on the peninsula (Rahders *et al*. 1997). The most alkaline-rich cold groundwaters are depleted in Ca with respect to the stechiometric ratio of calcium carbonate. In these waters, which are either saturated or oversaturated with respect to calcite, probably further addition of endogenous CO_2 and its titration to bicarbonate during water-rock interaction processes, leads to calcite precipitation.

Also the waters collected at the Ag. Nikolaos spring (samples from 4 to 8), which are the thermal waters least contaminated by seawater, fall on the calcium carbonate dissolution line (Figure 4b). On the contrary the remaining thermal water samples fall above this line evidencing an additional source of calcium. On a Ca vs. SO_4 binary diagram (Figure 4c) these samples plot on a line corresponding to the stoichiometric ratio of calcium sulphate dissolution. In the geology description of the area (Dietrich and Gaitanakis, 1995; Volti 1999) evaporitic rocks have never been described, but dissolution of hydrothermal anhydrite could explain the composition of these waters. Anhydrite is a common mineral in seawater dominated hydrothermal systems (Bischoff and Seyfried 1978) and its presence, together with other sulphate minerals, has been documented in the hydrothermal alteration products found at

Methana (Rahders *et al*. 1997).

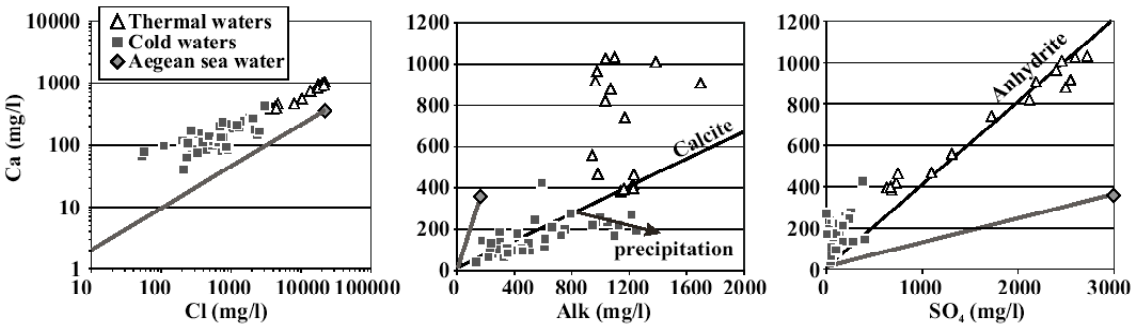

Figure 4 – Calcium vs. (a) Chloride, (b) Alkalinity and (c) Sulphate binary diagrams.

4. Conclusions

The main process affecting the salinity content of the groundwaters of Methana is mixing between a meteoric and a seawater component. Such a process could be considered natural in origin due to the fact that the peninsula of Methana can be assimilated to a small island and as such affected both by direct seawater intrusion and by sea-spray deposition. Thermal waters display the highest proportions of seawater component (up to nearly 100%). Seawater intrusion in the thermal aquifer is probably due to convective phenomena, while salinization of the cold aquifer due to over-abstraction is only a limited problem.

During their underground circulation water-rock interaction processes, enhanced by abundant endogenous CO_2 dissolution, modify the groundwaters' composition. Nearly all samples display, in fact, ion/chloride ratios higher than those obtained from simple seawater addition. The chemical evolution of the waters is therefore modified by the dissolution of primary minerals of the aquifers' rocks. Sometimes also dissolution of secondary hydrothermal minerals (calcite and anhydrite) contributes to the chemistry of the thermal water. Finally, precipitation of secondary minerals has only limited impact on water chemistry.

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